

Chain Conformation in Fluids and Nanopores

Noria Arab^{1,*}, Amina Negadi^{1,2}, Arti Dua², Thomas A, Vilgis²

¹ *University Aboubakr Belkaid of Tlemcen, Tlemcen, Algeria*

² *Max Plank Institut fur Polymerforschung, Ackermannweg 10, Mainz, Germany*

The conformational behavior of polymers in a critical solvent is mainly governed by two length scales, the chain length and the correlation length of the solvent density fluctuations [1,2]. Far away from the critical point, the size of a polymer in a binary mixture of good solvents simply scales as $R \sim N^{3/5}$, where N is the number of monomers. Close to the critical point, when the correlation length of the solvent density fluctuations is comparable to the chain size, the polymer collapses to form a globule of size $R \sim N^{1/3}$; a collapse transition close to the critical point is believed to be driven by the solvent density fluctuations, which induce attractive interactions between different parts of the chain. At the critical point itself, when the solvent density fluctuations act on a much larger scale compared to

the polymer size, the chain regains its original size, that is, $R \sim N^{3/5}$.

The fact that the solvent density fluctuations are instrumental in determining the bulk behavior of polymers in a critical binary solvent raises an important question when such a polymer mixture is present in a restricted geometry say a porous medium. In this case, the correlation length of the fluid stays finite and is mainly determined by the typical size of the tube. The question as to how a given confinement controls the conformational behavior of the polymer is an important one.

The idea is to determine the effective potential exerted on a chain under various conditions of temperature and fluid composition using the Edwards Hamiltonian formalism which is given by [1,3]:

$$\beta H = \frac{3}{2a^2} \int_0^N \left(\frac{\partial R(s)}{\partial s} \right)^2 ds + \frac{1}{2} \nu \int_0^N ds \int_0^N ds' \delta(R(s) - R(s')) + (\nu_1 - \nu_2) \sum_K \int_0^N ds \exp[-iKR(s)] c(K) + \beta H_f(c(r))$$

where $\beta H_f(c)$ can now be viewed as

$$\beta H_f(c(r)) = \int d^3r \left(\frac{1}{2} (\nabla c(r))^2 + \tau c^2(r) + \frac{\lambda}{4} c^4(r) \right)$$

The effective potential is given by

$$\tilde{v} = \nu_{mm} - \frac{(\Delta \nu)^2}{\tau + \left(\frac{a}{D}\right)^2}$$

where $(\Delta \nu)^2 = (\nu_1 - \nu_2)^2$.

The Hamiltonian can be transformed into a Flory free energy by simple dimensional analysis [4].

$$\beta F = \frac{R_{//}^2}{Na^2} + \tilde{v}(k_{//} = 0) \frac{N^2}{D^2 R_{//}}$$

Minimization of the above free energy yields the size of the chain in the nanopore.

$$R_{//} \approx \left(\nu_{mm} - \frac{(\Delta \nu)^2}{\tau + \left(\frac{a}{D}\right)^2} \right)^{1/3} N \left(\frac{a}{D} \right)^{2/3}$$

At the critical point, i.e., $\tilde{v} = 0$, the effective monomer-monomer potential \tilde{v} becomes negative when the tube diameter is sufficiently large:

$$\left(\frac{D}{b} \right)^2 \geq \frac{\nu}{(\Delta \nu)^2}$$

The size of the chain can be estimated by taking into account the three body interaction in the tube. The lateral extension is then given by:

$$R_{//} = \frac{a^4}{v_{mm} - \frac{(\Delta v)^2}{\tau + \left(\frac{a}{D}\right)^2}} N \left(\frac{a}{D}\right)^2$$

The effective interaction between the chain segments being attractive, the chain is expected to collapse inside the tube. In contrast to the bulk behaviour, where in a certain temperature regime the chain is always collapsed, the collapse in a confined geometry depends purely on material properties, the strength of the polymer–fluid interaction, the chain excluded volume, and the diameter of the tube. The geometry plays an important role in the collapse of a polymer chain in a critical fluid and the fluid with a finite correlation length.

References

- [1] T. A. Vilgis, A. Sans and G. Jannink, J. Phys. II (France) **3**, 1779 (1993)
- [2] F. Brochard and P.G. de Gennes, Ferroelectrics **30**, 33 (1980).
- [3] A. Negadi, A. Sans-Penninks, M. Benmouna and T.A. Vilgis, Macromol. Theory Simul. **8**, 285 (1999).
- [4] T. A. Vilgis, Phys. Rep. **336**, 167 (2000).